

# Synthesis and characterization of $(\text{La}_{1-x}\text{Sr}_x)_2\text{NiMnO}_6$

*A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF*

Master of Science in Physics

By

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## ***CERTIFICATE***

**THIS IS TO CERTIFY THAT THE THESIS ENTITLED “SYNTHESIS AND CHARACTERIZATION OF  $(\text{La}_{1-x}\text{Sr}_x)_2\text{NiMnO}_6$  SAMPLE” SUBMITTED BY Miss. SHYAMA MOHANTY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN PHYSICS AT NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA, IS AN AUTHENTIC WORK CARRIED OUT BY HER UNDER MY SUPERVISION AND GUIDANCE.**

**TO THE BEST OF MY KNOWLEDGE, THE MATTER EMBODIED IN THE THESIS HAS NOT BEEN SUBMITTED TO ANY OTHER ORGANIZATION.**

Date:

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## ***Abstract***

For the last two decades, double perovskite oxides have attracted many researchers as they exhibit interesting properties like multiferroicity.  $\text{La}_2\text{NiMnO}_6$  is an example of this type and shows ferromagnetic order near room temperature with high ferromagnetic transition temperature. In the present report,  $\text{La}_2\text{NiMnO}_6$  compound has been studied with strontium doping, synthesized through sol-gel route. XRD, resistivity measurements, magnetoresistance measurement and UV visible spectroscopy are done. XRD showed the presence of single phase in parent sample and appearance of secondary phase in 20% doped sample. Resistivity versus temperature was plotted to study its electrical behavior. Graph of  $\ln \rho$  and temperature inverse were plotted to calculate their activation energies. Percentage of magnetoresistance of the samples were calculated from the graphs. UV visible spectroscopy are also done to extract more information on the changing properties of LNM compound with various conditions.

# Chapter-1

## INTRODUCTION

### 1.1 Recent research on Oxides:

Oxides are regarded as a diversified class of materials which include the whole range from conductor to semiconductor to insulators and show a wide range of applications such as gas sensing, luminescence, antibiotics, catalysis, non-volatile memory and tunneling devices <sup>[2]</sup>. The diversified class of oxides comprises of superconducting oxides, ferroelectric oxides, magnetic oxides, multiferroic oxides etc. During the past decades, a lot of progress has been done on the synthesis, physical, chemical and structural characterization and a variety of applications has been discovered. The applications implicate both bulk and nano-forms. In present days, the selective exposure of high energy aspects at the surface of nanocrystallites is an important and challenging topic <sup>[1]</sup>.

#### 1.1.1 Superconducting oxides:

Transition-metal (TM) oxides are of great interest in physics because of superconductivity nature that arises due to electron correlations, with high critical temperature superconductivity. Until Bednorz & Muller reported superconductivity (1986) at ~23K in an oxide based compound, the superconducting phenomenon was considered only as low temperature physics having very less number of applications <sup>[6]</sup>. Then oxide based superconductors were discovered with superconducting transition temperature much higher than the temperature predicted by the theory. These types of superconductors are termed as high temperature superconductors (HTS). Example of a popular HTS is  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO). One can find profound applications of YBCO in magnetically levitated trains and magnetic resonance imaging for medical purpose <sup>[7]</sup>.

### **1.1.2 Ferroelectric Oxides:**

Materials exhibiting spontaneous electric polarization are known as ferroelectric materials and the phenomenon is called ferroelectricity. This property can be reversed by the application of an external electric field <sup>[4]</sup>. Oxides having ferroelectricity property are known as ferroelectric oxides. They have a vast collection of interesting properties and phenomena that have found widespread applications including electronics, micromechanics, and electrochemistry, both in bulk and thin films <sup>[5]</sup>. They are used as nonvolatile memory for their ferroelectric properties. They also exhibit piezoelectricity which makes them to be used in actuators and ultrasound imaging. Other application areas include tunable radio frequency devices, solid electrolytes, and solid state cooling <sup>[5]</sup>. Ferroelectric oxides are also stable in a wide range of mechanical, chemical and thermal conditions and can be fabricated using low-cost methods <sup>[8]</sup>. They show high dielectric constants which can be improved by suitable addition of dopants. Now a good number of ferroelectric oxides are synthesized which give above properties at room temperature. These oxides include BaTiO<sub>3</sub>, CaTiO<sub>3</sub>, PbTiO<sub>3</sub> and SrTiO<sub>3</sub> along with suitable dopants.

### **1.1.3 Magnetic Oxides:**

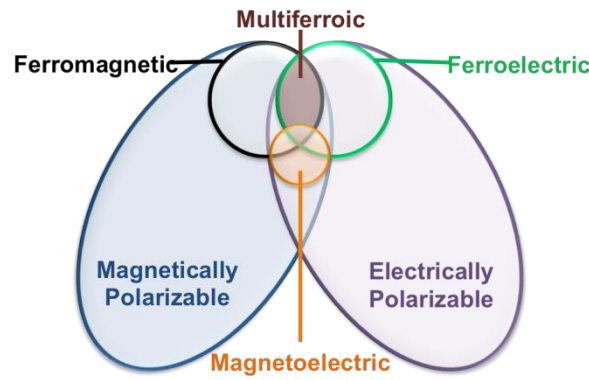
In the modern world, magnetic materials have vast applications in different fields in our day to day life. Ordinarily magnetic materials can be classified into two forms; soft and hard, considering the magnetic property. The soft magnets are the magnets having low coercivity in the hysteresis loop and the hard magnets have high coercivity. The magnetic oxides are generally soft magnets. Due to low coercivity, they find application in alternating magnetic field <sup>[6]</sup>. Other applications of these materials, both in bulk and thin film form, include permanent magnets, magnetic recording, AC magnets, RF control devices, microwave absorbers, EPR and FMR (medical), fiber optics superconductors, magnetoresistance and spintronics, etc <sup>[9]</sup>. They show excellent magnetic properties in high frequency as compared with metal magnetic materials. They have high electrical resistivity and smaller eddy current loss. These soft magnetic oxides generally exist in the forms of ferrites, manganites and cobaltites. They exhibit properties

like high curie temperature, high permeability and high stability. Transition metals like iron (Fe), cobalt (Co), manganese (Mn) and nickel (Ni) combining with oxygen and other materials results various oxides showing interesting phenomena like magnetodielectric, multiferroic <sup>[10]</sup>. The magnetic properties of iron oxides have achieved a broad range of applications including magnetic seals and inks, magnetic recording media, catalysts, and ferrofluids, as well as in contrast agents for magnetic resonance imaging and therapeutic agents for cancer treatment <sup>[11]</sup>.

#### **1.1.4 Multiferroic Oxides:**

Complex perovskite oxides exhibit a wide range of properties, including magnetism, ferroelectricity, strongly correlated electron behaviour, superconductivity and magnetoresistance, which have been the research areas of great interest among the scientific and technological community. There exist very few materials which exhibit multiple functional properties, known as multiferroics <sup>[12]</sup>. Multiferroics are interesting because they exhibit simultaneously ferromagnetic, ferroelectric polarizations, ferroelasticity and a coupling between them. Due to the lattice coupling between the magnetic and electronic domains (the magnetoelectric effect), the magnetic polarization can be altered by applying an electric field; likewise the ferroelectric polarization can be switched by applying a magnetic field <sup>[14, 18]</sup>. As a consequence, multiferroics have attracted many researchers. These oxides have the unique properties of both ferromagnetism and ferroelectricity in a single crystal. This opens broader applications in transducers, magnetic field sensors and information storage industry. These include BiFeO<sub>3</sub>, BiMnO<sub>3</sub>, TbMnO<sub>3</sub>, TbMn<sub>2</sub>O<sub>5</sub>, YMnO<sub>3</sub>, LuFeO<sub>4</sub>. Among these oxides BiFeO<sub>3</sub> (BFO) is the only material which gives ferroelectricity and antiferromagnetism at room temperature <sup>[13]</sup>.





Venn diagram <sup>[15]</sup>

## 1.2 Multiferroics:

A multiferroic material is basically a material which exhibits either ferroelectric or ferromagnetic or ferroelastic ordering; a feature typically demonstrated by the presence of a well-defined hysteresis loop when the material is switched electrically, magnetically or mechanically <sup>[16]</sup>. More recently there has been another ordering mechanism proposed which is called as ferrotoroidic ordering. The multiferroic materials are either rare earth manganites or ferrites or transition metal perovskite oxides. The examples are  $\text{TbMnO}_3$ ,  $\text{TbMn}_2\text{O}_5$ ,  $\text{HoMn}_2\text{O}_5$ ,  $\text{LuFe}_2\text{O}_4$ ,  $\text{BiFeO}_3$ ,  $\text{BiMnO}_3$  and  $\text{YMnO}_3$ . Some non-oxides are also multiferroics such as  $\text{BaNiF}_4$  and spinel chalcogenides, e.g.  $\text{ZnCr}_2\text{Se}_4$ . Magnetoelectric coupling in the materials, on the other hand, is a more general phenomenon irrespective of the state of magnetic and electrical ordering. More recently, multiferroic materials have become of tremendous interests because of potential device applications. For example, one can have multi-state memory element or sensors which can be operated in multi-mode or spintronic devices. Other applications are as transducers, information storage technology (FeRAM and MRAM) <sup>[22]</sup>. However, there are challenges in finding a material that would act as a perfect multiferroic at room temperature. Most multiferroic materials are not naturally occurring and are made in the laboratory.

Recent reports classify the multiferroics into Type I and Type II multiferroics. Type I multiferroics are those materials in which the source of ferroelectricity and magnetism is different and the effects are fairly

independent of each other. In contrast, type II materials are those where magnetism causes the existence of ferroelectricity attributed to the strong coupling between two states. Multiferroics may be in the form of single-phase and exhibit piezoelectricity <sup>[25]</sup>. Hence, the search continues for new single-phase and composite multiferroic materials that exhibit high ordering temperatures, high coupling constant, low dielectric loss and low leakage current <sup>[17]</sup>.

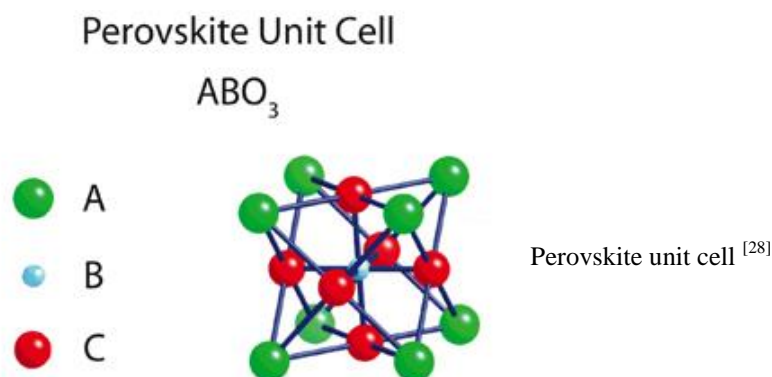
### **1.3 Magnetoelectricity:**

The magnetoelectricity (ME) effect is the phenomenon of inducing magnetic (electric) polarization by applying an external electric (magnetic) field <sup>[19]</sup>. The effects can be linear or/and non-linear with respect to the external fields. In general, this effect depends on temperature. The effect can be observed in single phase and composite materials. Some examples of single phase magnetoelectrics are  $\text{Cr}_2\text{O}_3$ . Some multiferroic materials show a coupling between the magnetic and electric order parameters. In composite materials the effect originates from interface coupling effects, such as strain <sup>[20]</sup>. Some of the promising applications of the ME effect are sensitive detection of magnetic fields, advanced logic devices and tunable microwave filters<sup>1</sup>. The primary magnetoelectric (ME) materials become magnetized when placed in an electric field and electrically polarized when placed in a magnetic field. In the secondary effect, the permeability or permittivity change is expected <sup>[21]</sup>.

### **1.4 Materials with Perovskite and Double Perovskite Structure:**

Perovskites are materials of the form  $\text{ABO}_3$ , where A is an alkaline earth or rare earth cation (Ca, Sr, La etc.), and B is an electronically active transition metal cation (Mn, Fe, Co, Ni, V, Cu etc.). The B ion is in an octahedral environment ( $\text{BO}_6$ ) while the A cations occupy the vacant space between the corner shared  $\text{BO}_6$  octahedra. Perovskite oxides have been intensely studied over the last few decades since they show a rich variety of magnetic, electrical and optical properties.

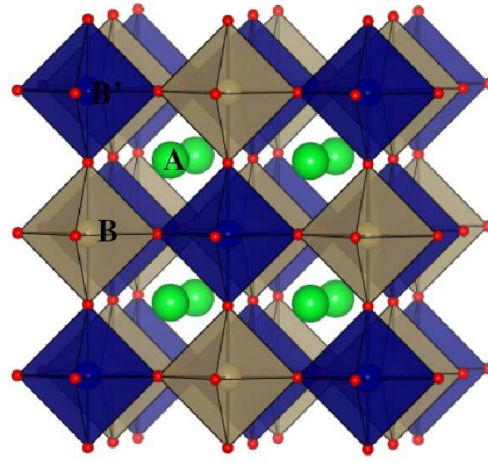
The perovskite family of oxides is the best studied family of oxides. The interesting thing about perovskites is the flexibility to accommodate almost all of the elements in the periodic system. Pioneering structural work on perovskites were conducted by Goldschmidt et al in the 1920s that formed the basis for further exploration of the perovskite family of compounds.



Coming to the crystal structure, perovskites are materials of the form  $ABO_3$ , while ‘double perovskites’ are of the form  $ABO_3 \cdot AB'O_3 \equiv A_2BB'O_6$ . The double perovskite structures have two kinds of octahedra;  $BO_6$  and  $B'O_6$ , repeating in all three directions, instead of only the  $BO_6$  octahedra as in perovskite. B and B' are electronically active transition metal cations, typically 3d, 4d or 5d elements, while A is either a rare earth or alkaline earth and controls the valence. Both B and B' are at the center of oxygen octahedra, i.e., are coordinated by six oxygen. In the structurally ordered double perovskite (DP) the B and B' should alternate along each cubic axis. However, unless the B and B' are very dissimilar ions, there is a significant possibility of disorderness. The B ion can occupy a B' site and vice versa. This aspect is completely absent in the simple perovskites where there is only one kind of ‘B site’. The magnetic order, however, is also strongly affected by the local ordering of B and B' ions <sup>[23]</sup>.

There has been enormous activity in the perovskite oxides over the last two decades, starting with the discovery of high  $T_c$  superconductivity, and this has inspired the study of these more complex, and potentially richer, double perovskites. The large number of possible B, B' combinations lead to a variety of electronic and magnetic phases. For example,  $Sr_2FeMoO_6$  has a high ferromagnetic  $T_c$  (420K), half-

metallic behavior, and large low field magnetoresistance (MR).  $\text{La}_2\text{NiMnO}_6$  has a dielectric anomaly arising from the structural modes, while  $\text{Sr}_2\text{CrOsO}_6$  and  $\text{Sr}_2\text{CrReO}_6$  show magneto-optical properties.



Double perovskite structure <sup>[29]</sup>

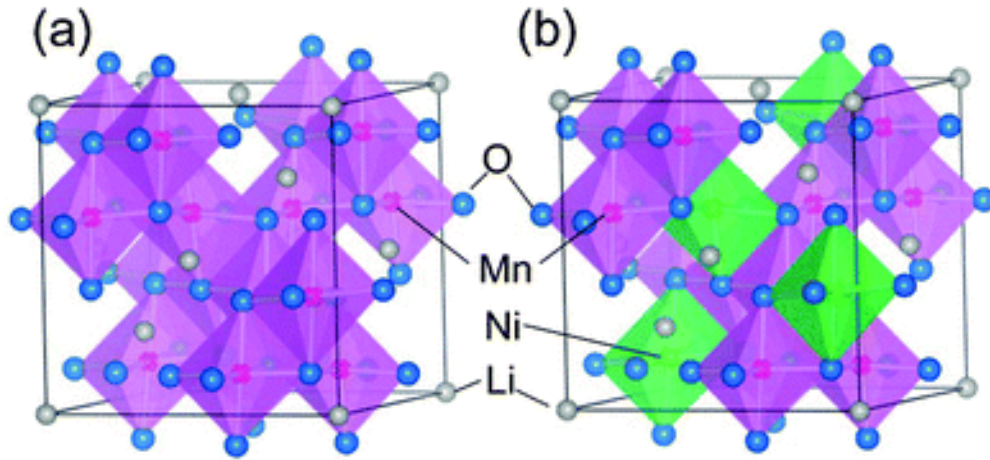
In perovskite structure, there is only one unit of  $\text{ABO}_3$ . For a substance to be multiferroic, there must be coexistence of magnetic moment for ferromagnetic and dipole moment for ferroelectric inside the unit cell which is difficult to occur in perovskite structure. But in case of double perovskite, there are two similar units of  $\text{ABO}_3$  which makes the two different moments (magnetic and dipole) compatible and easily tunable. So multiferroicity exists in double perovskite structure which is the major advantage of this type.

The rare earth perovskites have been widely studied using X-ray diffraction and neutron scattering techniques. Double perovskites are used as magnetic sensor applications since the discovery of tunnelling magnetoresistance (TMR) at room temperature and at low magnetic fields in powder samples of the ferrimagnetic double perovskites <sup>[22]</sup>.

## 1.5 Brief idea on $\text{La}_2\text{NiMnO}_6$

$\text{La}_2\text{NiMnO}_6$  popularly known as LNM, is a double perovskite oxide with interesting properties; magnetic, electronic and structural, which has enhanced its technical applications spectacularly. It has been identified as the first ferromagnetic insulators which has high ferromagnetic transition at 280K. Mn-O-Ni

superexchange interaction inside the perovskite structure gives rise to ferromagnetism in LNM. It also exists as magnetic semiconductor. Special property of LNM is that it exhibits magnetodielectric effect. Single phase LNM shows changes in the resistivity and dielectric properties due to the application of large magnetic field. Bulk LNM shows colossal magnetodielectric behavior. Therefore, it has found a wide scale of applications including spintronic devices, spin based transistors, solid state thermoelectric (Peltier) coolers.



Structure: LNM exists in ordered double perovskite structure.  $\text{NiO}_6$  and  $\text{MnO}_6$  form ordered octahedra which yield interesting magnetic, electrical and structural properties <sup>[23]</sup>. It exists in rhombohedral structure in high temperature and transforms to monoclinic structure with space group  $P2_1/n$  in low temperature with two structures coexisting over a wide range of temperature <sup>[24]</sup>. The structure depends on the arrangement of Ni and Mn. Ordering of Ni and Mn into distinguishable sites gives monoclinic structure whereas random distribution of Ni and Mn over octahedral sites of the perovskite structure shows rhombohedral structure <sup>[26]</sup>.

Synthetic conditions of LNM influence the atomic ordering of Ni and Mn which determines the magnetic ordering in the material.

## Chapter-2

### LITERATURE SURVEY

**1. Zhu *et al.*, Appl. Phys. Lett.100, 062406 (2012):**

- The ground states of  $\text{La}_2\text{NiMnO}_6$  are ferromagnetic semiconductors with alternative Ni/Mn ordering along the (1 1 1) direction.
- LNMO (1 1 0), LNMO (0 0 1) are ferromagnetic half metal and LNMO (1 1 1) is ferromagnetic semiconductor.

**2. Zhou *et al.*, Appl. Phys. Lett. 91, 172505 (2007):**

- Paramagnetic to ferromagnetic transition of LNM is observed at 280K.
- A bulk sample of LNM is prepared by solid state reaction and has an ordered double perovskite structure.
- Ni and Mn ions are ordered at the B site to a large extent.
- It has monoclinic structure with space group  $P2_1/n$ .

**3. GUO *et al.*, PHYSICS REVIEW B 77, 174423 (2008):**

- LNM thin films are grown over a wide range of oxygen pressure by Pulsed Laser Deposition method.
- Oxygen environment during synthesis has influence on crystal structure, chemical composition and magnetic properties.
- With increasing oxygen pressure during growth, paramagnet to ferromagnet transition temperature (280K) has become sharper.

**4. Nurissa *et al.*, Adv. Mater. 2005,17,2225-2227:**

- Stoichiometric amounts of metal nitrates are taken as precursors.

- Solution is evaporated and residue is dried at 400K for 1-2 days.
- Dielectric properties are found in LNM at temperatures as high as 280K.
- Nature of the sample is ferromagnetic.

**5. R.I. DASS *et al.*, PHYSICAL REVIEW B 68, 064415 (2003):**

- Sample is synthesized with Pechini method with  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .
- The coexistence of two ferromagnetic phases of comparable Curie temperatures; one monoclinic and other rhombohedral is shown.

**6. Iliev *et al.*, Appl. Phys. Lett. 90, 151914 (2007):**

- Raman spectra of epitaxial thin films of  $\text{La}_2\text{NiMnO}_6$  on (0 0 1) orientated  $\text{LaAlO}_3$  substrate have been investigated.
- Evolution of spectra with increasing temperature is consistent with a transition of monoclinic ( $\text{P}2_1/\text{n}$ ) to rhombohedral  $\text{R}\bar{3}$  structure.
- The thin films are synthesized by Pulsed Laser Deposition method.

**7. Lin *et al.*, Solid State Communication 149 (2009) 784-787:**

- Dielectric and conductivity characteristics of  $\text{La}_2\text{NiMnO}_6$  are investigated.
- Samples are found to be crystalized in monoclinic  $\text{P}2_1/\text{n}$  structure.
- Samples are prepared via solid state reaction process.

**8. Zhao *et al.*, J. Appl. Phys. 106, 123901 (2009):**

- Structure and magnetic properties of LNM nanoparticles with sizes ranging from 16 to 66nm are studied.
- Samples are synthesized by sol-gel method.
- Rate of disordered phase increases as particle size decreases.
- Saturation magnetization occurred at 4K.

**9. M. Hashisaka *et al.*, Journal of magnetism and magnetic materials 310**

**(2007) 1975-1977:**

- Ferromagnetic semiconductor  $\text{La}_2\text{NiMnO}_6$  are used as a barrier in tunneling junction.
- Junction with a ferromagnetic electrode showed magnetoresistance (MR) of -0.12% at 150K.

**10. Singh, Turong and Fournier, Appl. Phys. Lett. 91, 042504 (2007):**

- Epitaxial films of  $\text{La}_2\text{CoMnO}_6$  are grown on substrates.
- It shows ferromagnetic Curie temperature around 225K and insulating behavior.

**11. Yang *et al.*, J. Appl. Phys. 111, 084106 (2012):**

- $\text{La}_2\text{Ni}(\text{Mn}_{1-x}\text{Ti}_x)\text{O}_6$  ceramics are synthesized by solid state reaction process.
- It gave monoclinic structure with P21/n which permitted ordering of Ni/Mn.
- Ti substitution for Mn strongly affects the crystallographic, magnetic and dielectric properties of  $\text{La}_2\text{NiMnO}_6$ .
- The  $T_c$  and spontaneous magnetization or FM component decrease with increase in Ti concentration.



## Chapter-3

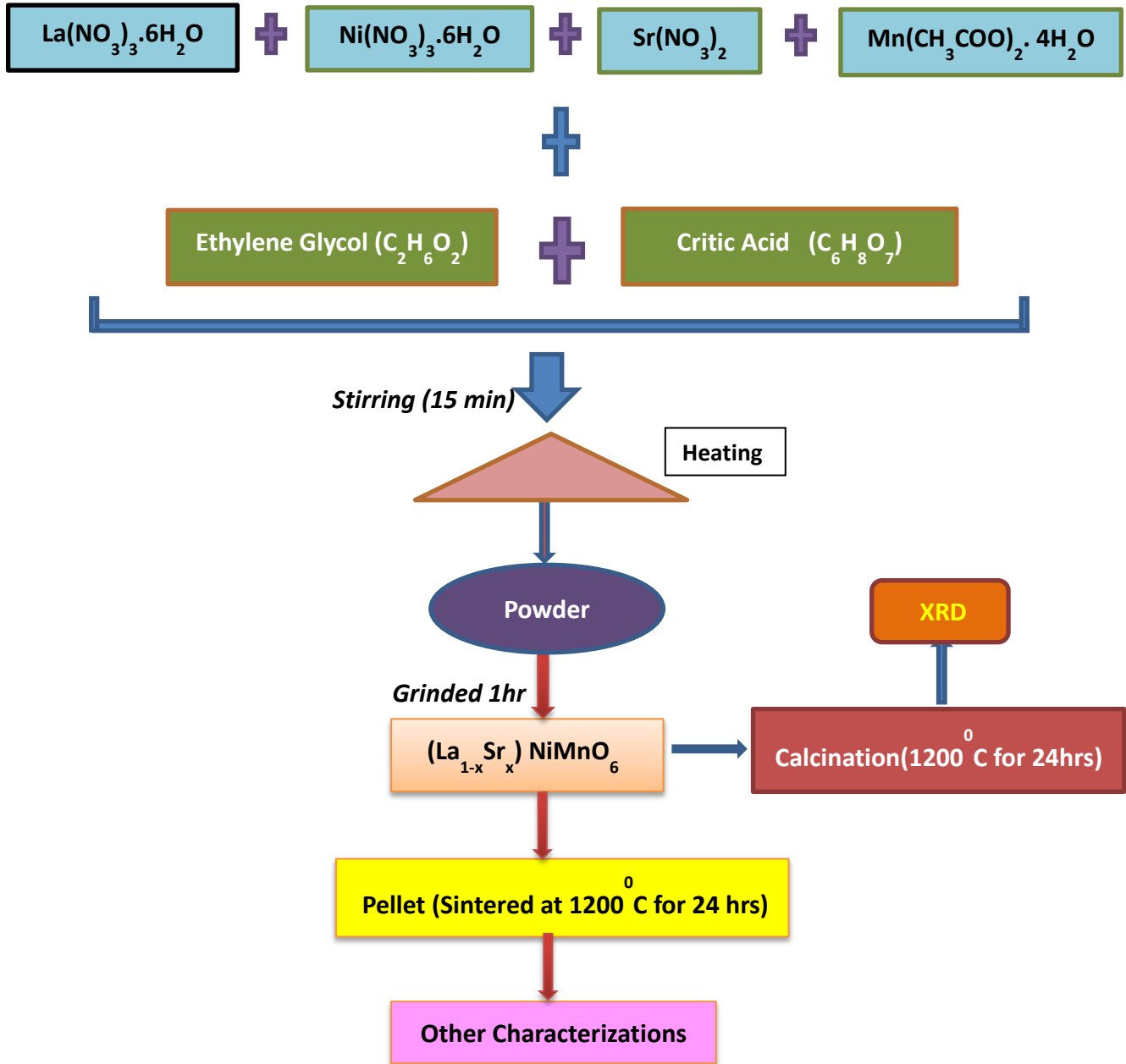
# EXPERIMENTAL DETAILS

### 3.1 Synthesis:

The  $(\text{La}_{1-x}\text{Sr}_x)_2\text{NiMnO}_6$  samples are prepared in sol gel route. Stoichiometric amount of lanthanum nitrate  $(\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$ , nickel nitrate  $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ , manganese acetate  $(\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O})$  and anhydrous strontium nitrate  $(\text{Sr}(\text{NO}_3)_2)$  were taken as precursors. A beaker, spatula and a piece of aluminium foil are cleaned with acetone for measurement. 1M citric acid and ethylene glycol are taken as chelating agents. Few drops of concentrated Nitric acid  $(\text{HNO}_3)$  are poured into the solution to make manganese acetate dissolved in water and to maintain the pH. An emerald green colored solution of all precursor is obtained and heated in hot plate with continuous stirring. After 2 to 3 hours, due to continuous evaporation of water, an emerald color gel at the bottom of the beaker is obtained. The gel is formed with a fluffy blackish powder. The collected powder from the beaker is grinded for about one hour with mortar pestle. Then from the powder sample, two to three pellets of 10mm diameter are prepared by dry pressing method with  $50\text{kg/m}^2$  pressure applied for two minutes. All the prepared pellets along with the remaining powder sample are calcined at  $1200^\circ\text{C}$  for 24 hours.

The exact procedure is given in the next page.

### 3.2 Flow Chart:



## Chapter-4

# RESULTS AND DISCUSSIONS

### 4.1 XRD:

In order to understand the phase purity of the sintered samples, X – Ray diffraction (XRD) was carried for all three compositions. XRD data was collected in Rigaku Ultima – IV system, with the angular range  $20^{\circ}$ -  $80^{\circ}$  at a scanning rate of  $3^{\circ}/\text{min}$ . XRD pattern of parent LNM is shown in Fig.1. All the peaks could be indexed to LNM phase. No extra peaks were seen. Hence the sample is single phase and is devoid of any other secondary phases. The observed pattern is indexed to the monoclinic structure with space group P21/n. Reitveld refinement of XRD data for LNM (not shown) is carried out for structural analysis. The observed structural parameters are calculated to be  $a= 5.45483 \text{ \AA}$ ,  $b=5.50038 \text{ \AA}$   $c=7.73048 \text{ \AA}$  and  $\alpha = 90^{\circ}$ ,  $\beta = 89.93^{\circ}$ ,  $\gamma = 90^{\circ}$ .

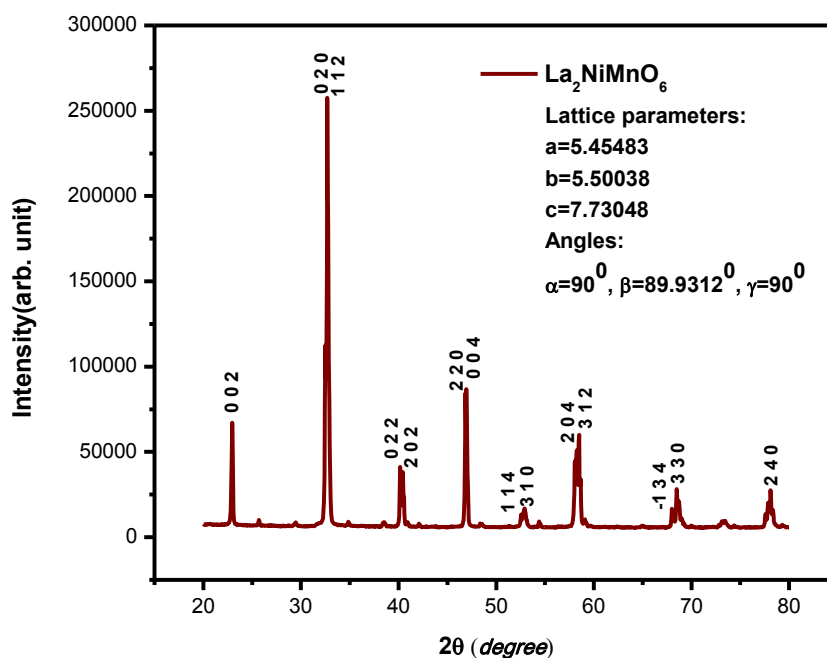


Fig. 1: XRD pattern of LNM

XRD data for all three compositions are plotted in a combined plot in Fig.2. With 10% Strontium (Sr) substitution, some peaks are disappeared in the data signaling some structural modification. The modified structure is yet to be understood completely. For 20% of Strontium substitution appearance of extra peaks near  $37^\circ$  and  $43^\circ$  indicates the possibility of secondary phases. The secondary phase is yet to be identified. Since  $\text{Sr}^{+2}$  (132pm) is having large ionic radius than  $\text{La}^{+3}$  (117.2pm), so substitution of  $\text{Sr}^{+2}$  at  $\text{La}^{+3}$  - site might be affecting the tolerance factor of the compound. The tolerance factor of the compound determines the stability of perovskite phase for a given set of anions and cations. Therefore it may be concluded that 20%  $\text{Sr}^{+2}$  substitution at La site is exceeding the solubility limit of the compound hence leading to secondary phase.

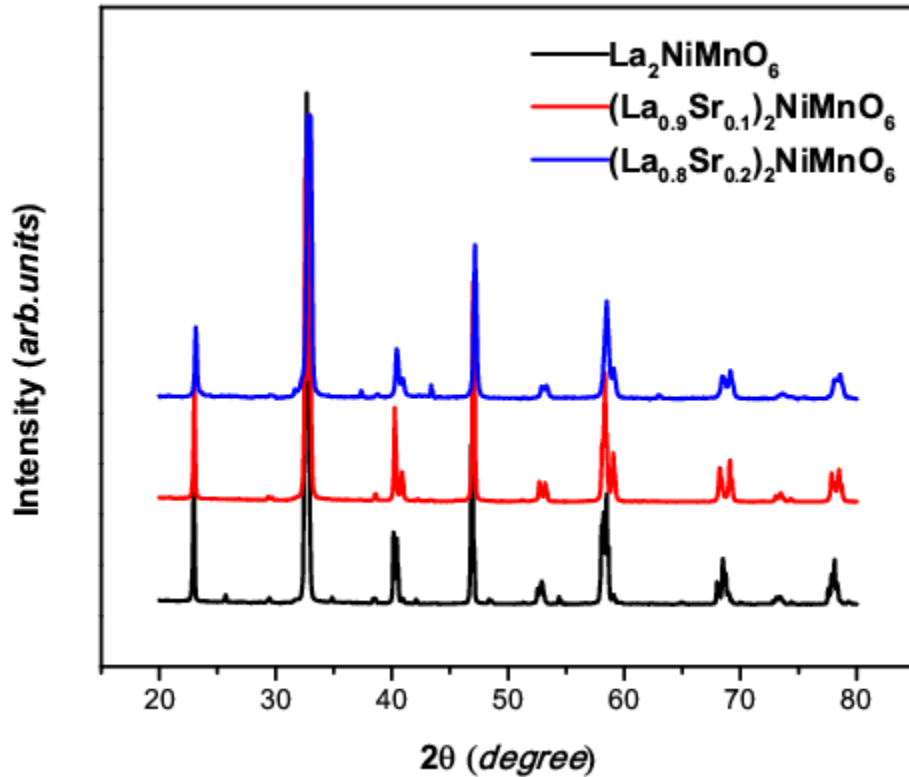


Fig. 2: XRD patterns of Sr doped samples with parent sample

## 4.2 Resistivity Measurement:

The DC electrical behavior of the sample is studied by two probe resistivity method. Low temperature resistivity is measured by Keithley 6517B electrometer equipped with Janish make Closed Cycle Refrigerator (CCR) and Lakeshore 331 temperature controller. The resistivity is measured in the temperature range 300K – 30K in cooling mode. The room temperature resistivity decreases with increased Sr – concentration (See Fig. 4). Temperature dependent resistivity behavior of all three compositions shows the semiconducting nature of the compounds. The resistivity data is plotted in log scale for better resolution. It was observed from the data that 10% Sr substituted sample is somehow untrendy and show a crossover of resistivity with 20% substituted sample. The crossover of resistivity may be related to the structural modification as depicted from XRD data.

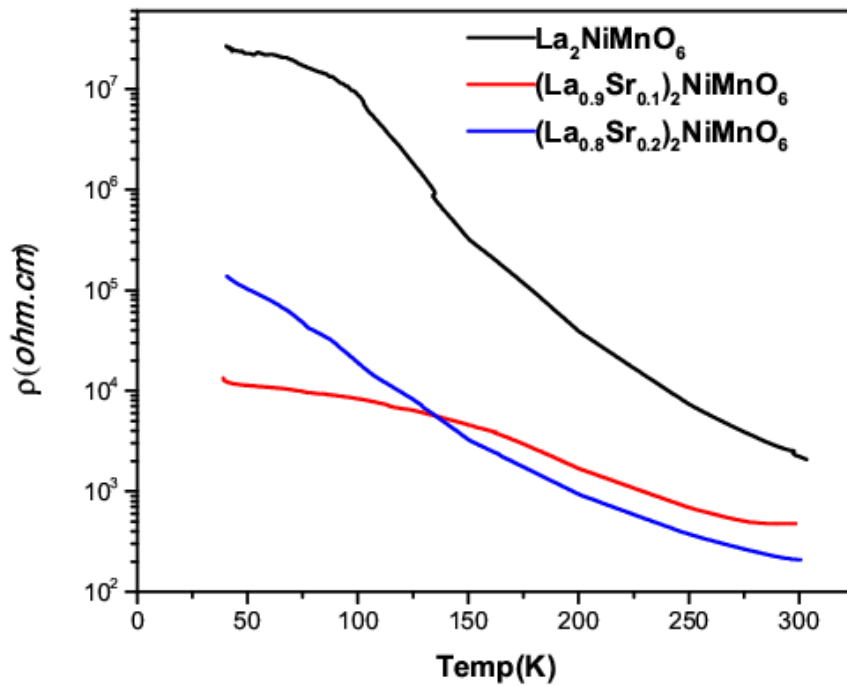


Fig. 4: Resistivity vs temperature graph

In order to have a greater insight on the conduction mechanism involved, the resistivity data is analyzed critically. The first understanding of monotonic increase in resistance with decrease in temperature, leads to a thermally activated behavior. Thermally activated behavior is obtained when resistivity obeys the Arrhenius equation

$$\rho = \rho_0 \exp\left(\frac{-E_a}{KT}\right)$$

Fig 5.a.b.c show the plot  $\ln \rho$  vs  $1/T$ . The slope of the linear fit to the experimental data gives the activation energies. The red lines show the linear fits to different temperature ranges of resistivity data. Resistivity of LNM is linearly fitted in three different temperature ranges with activation energies 0.152eV, 0.09842eV, 0.068eV. Similar fitting in 10Sr and 20Sr gives activation energies 0.08eV, 0.061eV, 0.022eV and 0.079eV, 0.059eV, 0.039eV respectively.

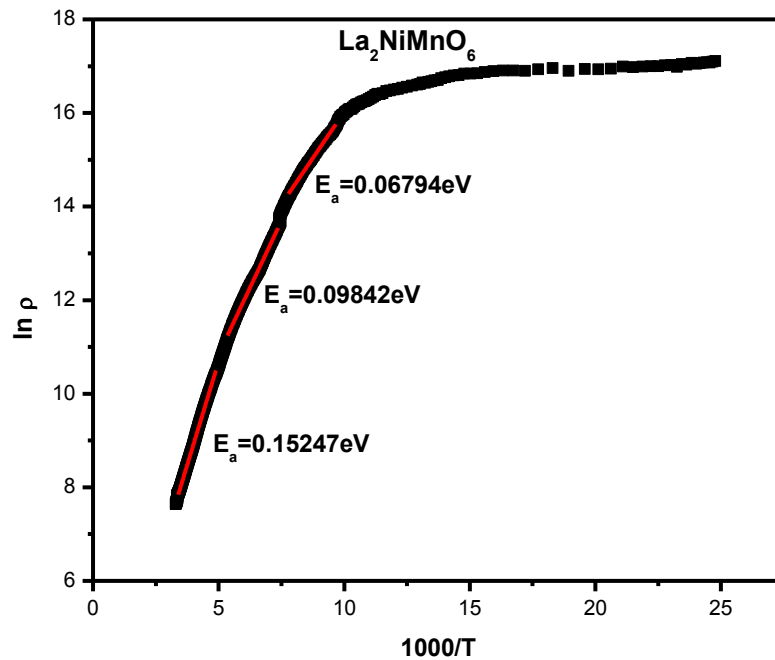


Fig. 5a: Activation energy calculation of LNM

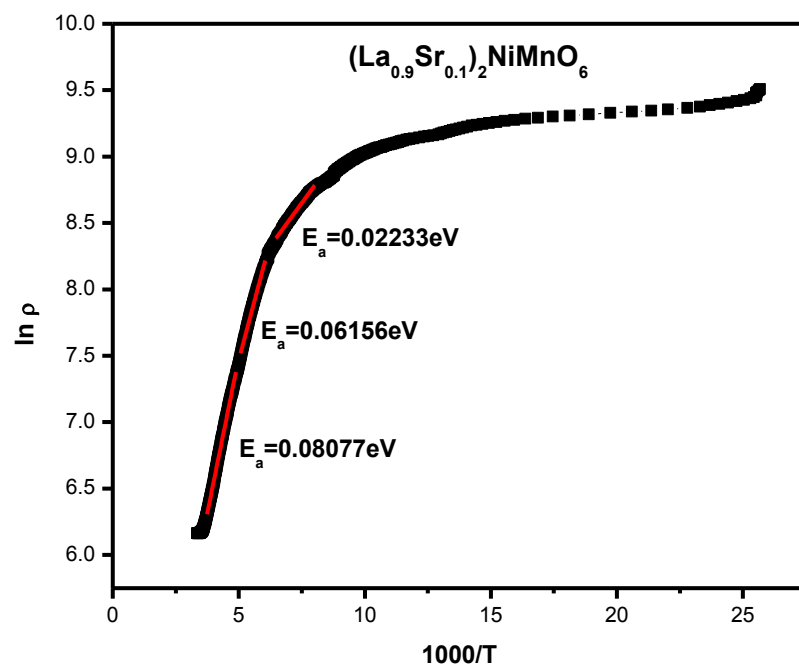


Fig. 5b: Activation energy calculation for 10 Sr doped sample

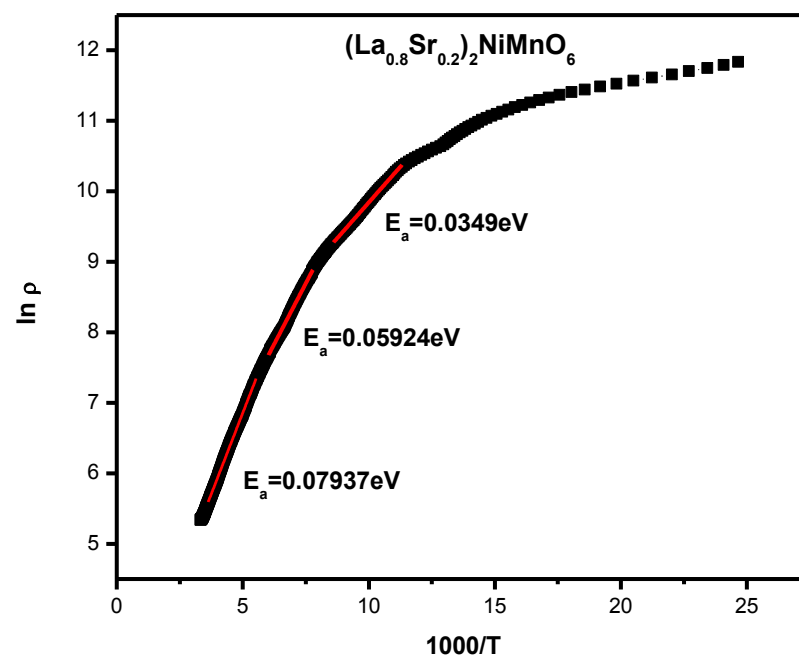


Fig. 5c: Activation energy calculation for 10 Sr doped sample

### 4.3 Magnetoresistance Measurement:

Several literatures talks about the magnetoresistive behavior of LNM and  $(\text{La}_{1-x}\text{Sr}_x)_2\text{NiMnO}_6$ . Room temperature magnetoresistance is measured by applying a magnetic field to the sample through an electromagnet (GMW make). Two probe resistivity was measured by Keithley 6517B electrometer in varying magnetic field. Fig.6 a, b, c show variations of resistivity with positive and negative direction of applied magnetic field. The resistivity of all samples is measured up to four cycles of measurement. From the plots the samples clearly show hysteresis in resistivity value. Another significant observation is made which is, the resistivity value decreases (negative magnetoresistance) with increase in magnetic field for LNM. In case of 10Sr and 20Sr the resistivity value is increased by increasing the magnetic field (positive magnetoresistance). This significant observation is yet to be understood.

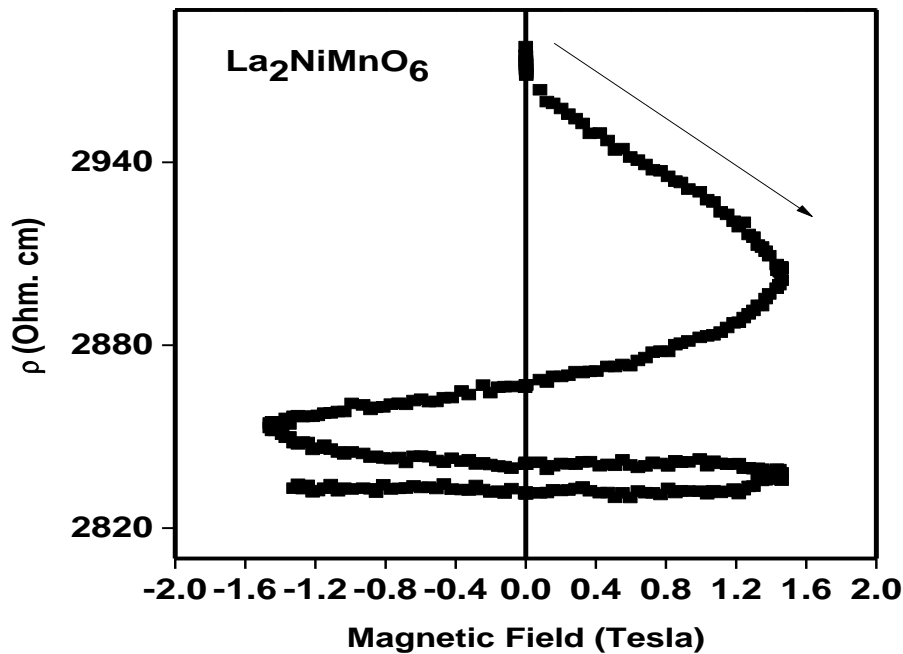


Fig. 6a: Negative magnetoresistance of LNM



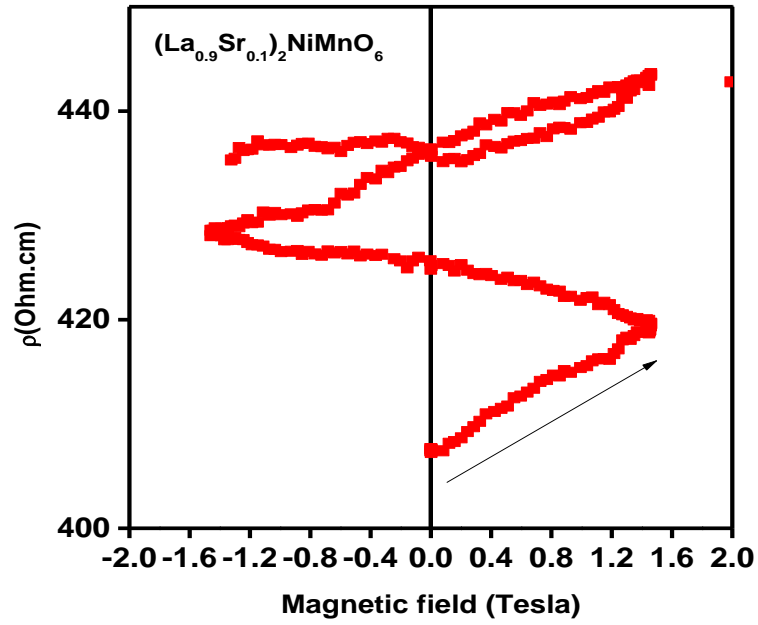


Fig. 6b: Positive magnetoresistance of 10Sr doped sample

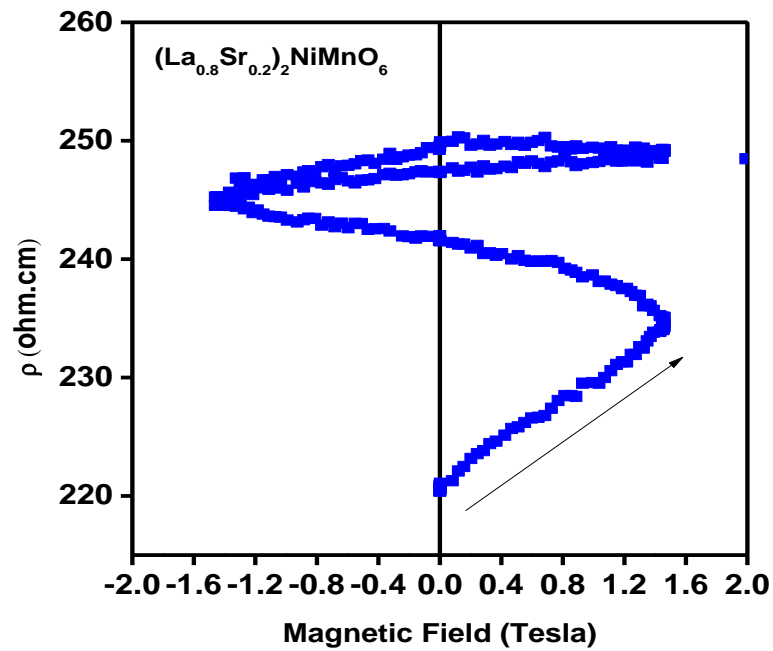


Fig. 6c: Positive magnetoresistance of 20Sr doped sample

For putting the magnetoresistance data in perspective, first positive half cycles of all three composition are selected. The percentage magnetoresistance is calculated from the following formula

$$\%MR = \frac{R(H) - R(0)}{R(0)}$$

Fig.7 show the percentage magnetoresistance vs magnetic field for all the three compositions. In the plot black line represents the data for LNM and red and blue are representing 10Sr and 20Sr. %MR is negative for LNM and is positive for 10Sr and 20Sr. It is observed from the plot that with increase in Sr - content, % change of MR increases. For LNM, %MR change is 2.5% at a field of 1.4T in negative axis. With 10% Sr doping, %MR is increased to 3.5% at 1.4T field and with 20% Sr doping, it is up to 7%MR at the same applied field has been observed.

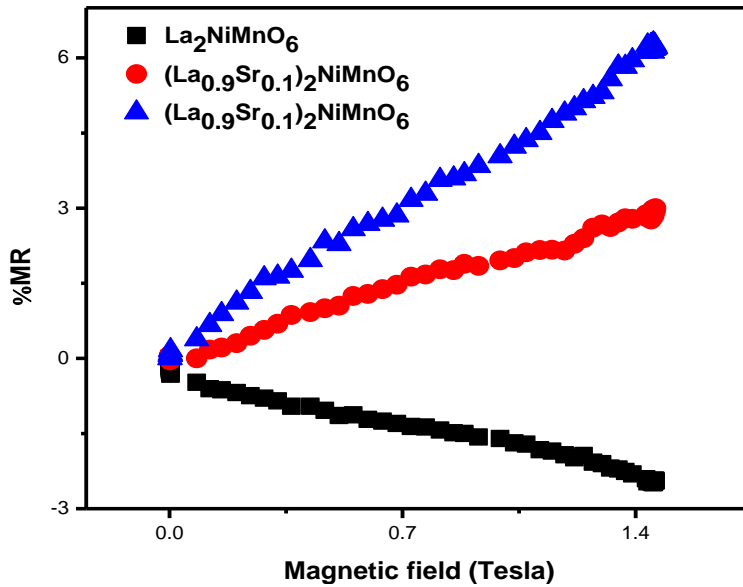


Fig. 7: Comparison of %MR of different samples

#### 4.4 UV Visible Spectroscopy:

In the reported literature, it has been observed that LNM has about 1eV band gap which corresponds to about 1200nm wavelength. This range of wavelength for characterization is not available with us. So the spectrograph does not give any information to calculate the band gap energy of LNM semiconductor. But

in the scanning range of 400nm to 800nm in reflection mode, we can observe that reflectance increases with increase in Sr doping. Increase in reflection is an indication of increased electrical conductivity due to Sr doping. As  $\text{Sr}^{2+}$  in the lattice may lead to increase in hole concentration, these holes might be responsible for increased reflectivity.

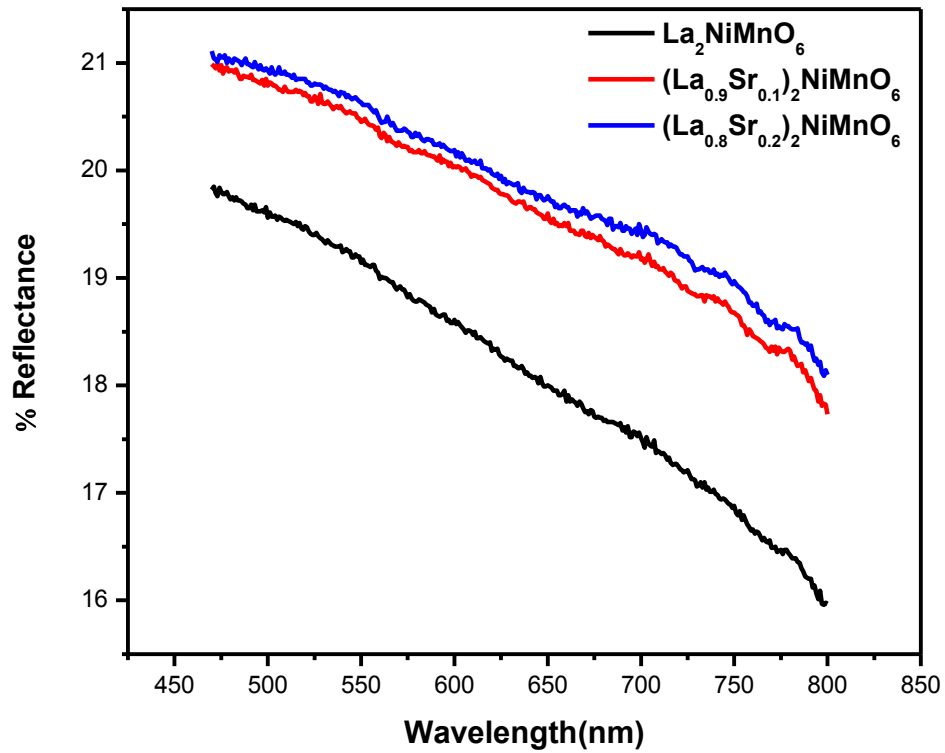


Fig. 8: UV Visible spectrograph of all the prepared samples

## Chapter-5

### CONCLUSION

Samples of  $\text{La}_2\text{NiMnO}_6$  along with 10% and 20% strontium doping are prepared by sol-gel combustion route. The samples are characterized by XRD which has given information about the phase of the sample. In parent sample LNM, single phase has been observed. In 10% doping of strontium, we observe some peaks are diapered. It may happen due to some structural change in the material. In the 20% doped sample, some extra peaks are observed which correspond to secondary phase. Then electrical characterizations are done to investigate its electrical properties. Graphs between resistivity and temperature are plotted. It is observed that with decrease in temperature, resistivity increases for the three prepared samples. In the graph, we can also observe that there is crossing over between 10% Sr doping and 20% Sr doping. This may happen due to the presence of impurity phase in 20% Sr doped sample. Thus it shows thermally activated behavior near room temperature. For further investigation, activation energies of the samples are calculated. It is seen that with increase in the concentration of Sr in the parent sample, activation energy decreases which implies that the sample becomes conducting with increased value of Sr doping. Then in the presence of magnetic field, the change in resistivity has been investigated at constant room temperature. Graphs between resistivity and magnetic field are plotted. LNM shows negative magnetoresistance whereas strontium doped samples showed positive magnetoresistance. A graph has been plotted in between % MR change and magnetic field to compare the property. It is seen that with increase in Sr doping, %MR increases. Also UV visible spectroscopy has been done for each sample. Plotting graph between reflectance and wavelength, we find reflectance increases with increase in strontium concentration. In our experiment, we find with strontium doping, the sample becomes conducting.

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